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(54) Optical recording medium and optical recording apparatus

(57) A phase change type optical recording medium has at least a first dielectric layer, a first boundary layer, a recording layer, a second boundary layer, an absorption correction layer and a reflection layer in this order on a substrate. The recording layer has a specific composition of the formula

$$[\{(Ge_{1-k}Sn_k)_{0.5}Te_{0.5}\}_x(Sb_{0.4}Te_{0.6})_{1-x}]_{1-y}Sb_yA_z$$

where A is an element of any of the groups 3-14 of the 3rd-6th period of the periodic table, excluding Ga, Sb and Te; and x, y,z and k are in ranges respectively represented by formulae (1) or (2):

$$0.5 \le x \le 0.95;\ 0 \le y \le 0.08;\ 0 \le z \le 0.2;\ k = 0 \quad (1)$$

$$0.5 \le x \le 0.95\ 0.01 \le y \le 0.08;\ z = 0;\ 0 \le k \le 0.5 \quad (2)$$

The first and second boundary layers are respectively mainly composed of at least one of carbon, carbides, oxides and nitrides, and the absorption correction layer has a refractive index of 1.0 to 4.0 and an attenuation coefficient of 0.5 to 3.0.

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Description

[0001] This invention relates to an optical recording medium and an optical recording apparatus that allow information to be recorded, erased and reproduced by irradiation with a laser beam. Particularly, this invention relates to a rewritable phase change type optical recording medium that allows information signals to be recorded at high speeds and high densities.

[0002] A rewritable phase change type optical recording medium has a recording layer mainly composed of tellurium, etc., and at the time of recording, the recording layer in the crystalline state is irradiated with focused laser beam pulses for a short time, to be rendered partially molten. The molten portion is quickly cooled by thermal diffusion and solidified, to form recorded marks in an amorphous state. The light reflectance of the recorded marks is lower than that of material in a crystalline state and can be optically reproduced as recorded signals. For erasure, the mark portions are irradiated with a laser beam, to be heated to a temperature lower than the melting point of the recording layer and higher than the crystallization temperature, for crystallizing the recorded marks in the amorphous state for return into the original non-recorded state. As the materials of recording layers of such rewritable phase change type optical recording media, alloys such as $Ge_2Sb_2Te_5$ (N. Yamada et al., Proc. Int. Symp. on Optical Memory, 1987, p.61-66) are known.

[0003] In an optical recording medium using a Te alloy as the recording layer, the crystallization rate is high, and simply by modulating the irradiation power, high speed overwriting by one circular beam can be executed. In an optical recording medium using such a recording layer, usually, one of each of a heat resistant and translucent dielectric layer is formed on both the sides of the recording layer, to prevent the recording layer from being deformed or opened at the time of recording. Furthermore, a technique in which a light-reflecting metallic reflection layer of light-reflecting Al, for example, is laminated on the dielectric layer on the side opposite to the incident optical light falling side, to improve the signal contrast at the time of reproduction by an optical interference effect is known.

[0004] The rewritable phase change type optical recording medium presents a problem regarding the repetition durability of the disc, in that repeated overwriting causes the reproduced signal amplitude (contrast) to decline, thus aggravating the jitter characteristics or causes a burst defect due to delamination or breaking of the protective layer. As a means for improving the repetition durability, it is known to form a diffusion prevention layer in contact with the recording layer, for example, as described in JP-A-11-115315.

[0005] However, as the optical recording medium becomes higher in linear velocity and higher in density, there arises a problem in that the erasure characteristics are impaired in the conventional optical recording medium. That is, if overwrite recording is carried out on a track having already recorded signals, the forms and positions of recorded marks are modulated by the signals existing before overwriting, to impair the erasure characteristics. As a result, there arises a problem in that, as compared with the recording of the first time, the jitter characteristics are aggravated.

[0006] As a means for improving the erasure characteristics, a technique for forming an absorbable layer for absorbing the light transmitting the recording layer is proposed, for example, in JP-A-5-159360. However, the absorbable layer proposed here, which is composed of a metal such as Ti, Ni, W, Mo, V, Nb, Cr or Fe, is unsatisfactory as a means for improving the erasure characteristics.

[0007] Furthermore, as the optical recording medium becomes higher in linear velocity and higher in density, there arises a problem in that since the recorded marks become smaller in size, the signal contrast becomes lower, so aggravating the jitter.

[0008] Moreover, when using conventional optical recording media, if a disc having signals recorded is allowed to stand for a long time, the recorded marks vanish. Furthermore, if an optical recording medium having signals recorded thereon is allowed to stand for a long time and has other signals overwritten thereon, the jitter characteristics may be aggravated as compared with a case of immediate overwriting. Thus, the optical recording medium presents a problem regarding storage durability.

[0009] Furthermore, the phenomenon known as cross erasure, whereby if the track width is narrowed to achieve a higher density, a laser beam also acts on an adjacent track, to affect the recorded marks in the adjacent track, thus aggravating the jitter characteristics is also a serious problem. This problem becomes more serious especially when the track width is 0.7 x d (d is the laser beam diameter on the recording surface) or less.

[0010] A problem may also arise in that if a laser beam is repetitively applied for reproduction, the recorded marks are partially crystallized, so deteriorating the signal quality (so-called reproducing light deterioration). In an optical recording medium with a higher crystallization rate for allowing higher linear velocity recording, the problems of cross erasure and reproducing light deterioration are more likely to occur.

[0011] The invention addresses the problem of providing a rewritable phase change type optical recording medium and an optical recording apparatus that have good erasure characteristics and small jitter, which are unlikely to cause cross erasure and'reproducing light deterioration and which also have good storage durability even if recording is executed at a high linear velocity at a high density. '

[0012] According to this invention there is provided an optical recording medium which allows information to be recorded, erased and reproduced by laser beam irradiation, and in which the recording and erasure of information are

achieved by reversible phase change between an amorphous phase and a crystalline phase, characterized in that at least a first dielectric layer, a first boundary layer, a recording layer, a second boundary layer, an absorption correction layer and a reflection layer are provided in that order on a substrate, that the composition of the recording layer is represented by general formula

$$[\{(Ge_{1-k}Sn_k)_{0.5}Te_{0.5}\}_x(Sb_{0.4}Te_{0.6})_{1-x}]_{1-Y}\,Sb_yA_z$$

where A is an element belonging to any of the groups 3 - 14 inclusive of the 3rd - 6th period inclusive of the periodic table, excluding Ge, Sb and Te; and x, y, z and k are in ranges respectively represented by the following formulae (1) or (2)

$$0.5 \leq x \leq 0.95,\ 0 \leq y \leq 0.08,\ 0 < z \leq 0.2,\ k = 0 \tag{1}$$

$$0.5 \leq x \leq 0.95,\ 0.01 \leq y \leq 0.08,\ z = 0,\ 0 \leq k \leq 0.5 \tag{2}$$

that the first boundary layer and the second boundary layer are respectively mainly composed of at least one of carbon, carbides, oxides and nitrides, and that the absorption correction layer has a refractive index of 1.0 to 4.0 and an attenuation coefficient of 0.5 to 3.0.

[0013] Another aspect of this invention provides an optical recording apparatus, having an optical head and an optical recording medium, in which a laser beam is applied from the optical head to allow information to be recorded, erased and reproduced by reversible phase change between an amorphous phase and a crystalline phase in the optical recording medium, characterized in that the linear velocity of laser beam irradiation is $7.5 \times 10^6 \times d$ (d is the laser beam diameter on the recording surface) or more per second, that the length of the shortest mark of the recorded marks recorded according to the mark edge method by the laser beam is $0.55 \times d$ or less in the laser beam propagation direction, that the track width of the optical recording medium is $0.7 \times d$ or less, and that the optical recording medium is the above-mentioned optical recording medium.

[0014] In this invention, "mainly composed of" means that the ingredient concerned is present in an amount of 50 wt% or more, by weight of the total layer, in the layer concerned. It is more preferable that the ingredient concerned is present in an amount of 80 wt% or more in the layer concerned.

[0015] The laser beam diameter d refers to the diameter at which the intensity becomes $1/e^2$ of the central intensity in a laser beam with intensities distributed according to the Gaussian distribution.

[0016] It can be considered that one of the causes of the problem that the erasure characteristics are not good is that since the difference between the reflectance of the recorded mark portions of the amorphous state and the reflectance of the region of the crystalline state in the recording layer is large, the quantity of light absorbed by the recorded mark portions of the amorphous state becomes larger than the quantity of light absorbed by the region of the crystalline state. As a result, it can be considered that since the pre-recorded mark portions are heated quickly during the recording with a laser beam, the overwritten signals are modulated by the signal components existing before overwriting, to lower the erasure rate.

[0017] If an optical recording medium having signals recorded is allowed to stand for a long time, the reproduced signal intensity may decline and the overwriting jitter deteriorates considerably. It can be considered that the possible causes of the phenomena are that since the optical recording medium is allowed to stand for a long time, the recorded marks of the amorphous state change, for example, in atomic arrangement or that the dielectric layer and the recording layer are caused to react with each other.

[0018] It is considered that the causes of the cross erasure and the reproducing light deterioration are that since the light absorptivity in the amorphous region of the recording layer is higher than the light absorptivity in the crystalline region, the recorded mark portions are likely to rise in temperature, and that since a recording layer composition with a high crystallization rate is used to allow high linear velocity recording, the recorded marks are crystallized even by a low laser power such as the end of a laser beam or reproducing light.

[0019] We conducted intensive studies and found that the boundary layers provided in contact with the recording layer on both sides of it are effective for improving the erasure characteristics, reducing the overwriting jitter and improving storage durability, and also the reproduction characteristics and overwriting characteristics after long-term storage.

[0020] Furthermore, we found a recording layer composition large in the reflectance difference caused by phase change and stable in the amorphous phase, to allow both good jitter and good storage durability to be obtained. Furthermore, we found that the recording layer composition is effective also for decreasing the cross erasure and the

reproducing light deterioration.

[0021] Furthermore, by providing an absorption correction layer between the second boundary layer and the reflection layer and selecting the material of the absorption correction layer for specifying the optical constants, i.e., the refractive index and the attenuation coefficient, an optical design could be made to ensure that the ratio of the light absorptivity of the crystalline region of the recording layer to the light absorptivity of the amorphous region (Ac/Aa) becomes larger than the conventional ratio and that the reflectance difference between the crystalline region and the amorphous region also becomes larger. We found that this optical design allowed a high contrast and erasure characteristics to be obtained, and could improve the overwriting jitter further. They also found that the absorption correction layer could decrease the light absorption of the recorded mark portions and could reduce the influence of the beam falling at the time of recording on an adjacent track, to allow the cross erasure to be decreased. They also found that the durability against the reproducing light deterioration could be improved greatly for the same reason.

[0022] The above technique could provide, for the first time, a rewritable phase change type optical recording medium having advantages in that the erasure characteristics are good while the jitter is small even in high linear velocity high density recording at a linear velocity of $7.5 \times 10^6 \times d$ (d is the laser beam diameter on the recording surface) or higher in laser beam irradiation and at a density such that the length of the shortest mark of the recorded marks recorded by a laser beam according to the mark edge method is $0.55 \times d$ or less in the laser beam propagation direction, that even if a substrate with a recording track width of $0.7 \times d$ or less is used, cross erasure is less likely to occur, that even if the laser beam is applied repetitively for reproduction, the signal quality is unlikely to deteriorate, and that the storage durability is also good.

[0023] Furthermore, the optical recording medium of this invention is also good in repetition durability, since the recording layer is kept between boundary layers.

[0024] Preferred embodiments of the invention are now described in more detail.

[0025] A typical layer constitution of the optical recording medium of this invention has a first dielectric layer, a first boundary layer, a recording layer, a second boundary layer, an absorption correction layer and a reflection layer laminated in this order on a transparent substrate. These layers are described below sequentially.

[0026] The first dielectric layer is provided for preventing the substrate from being damaged by heat during recording and for preventing the recording layer from being deformed or opened by heat. The materials that can be used for the first dielectric layer include inorganic compounds such as ZnS, SiO_2, silicon nitride and aluminum oxide. Especially a mixture consisting of ZnS and SiO_2 is preferable. Since this material is small in residual stress, it is unlikely to cause, for example, burst deterioration caused by repeated overwriting. Furthermore, a mixture consisting of ZnS, SiO_2 and carbon is especially preferable since it is further smaller in the residual stress of the film made of it and is unlikely to cause deterioration of, e.g., recording sensitivity, carrier-to-noise ratio (C/N) or erasure rate.

[0027] It is preferable that the first dielectric layer is 1.9 to 2.4 in refractive index and 0.1 or less in attenuation coefficient. Such a dielectric layer allows a design that ensures a high reflectance difference due to an optical interference effect. The thickness of the first dielectric layer can be decided having regard to optical conditions, but it is preferable that the thickness is 5 to 500 nm. If the thickness is above the maximum of this range, for example, cracking may occur. If the thickness is below the minimum of this range, the substrate may be thermally damaged by repeated overwriting, and the repetition characteristics may deteriorate. An especially preferable range of thickness is 50 nm to 200 nm.

[0028] In this invention, a respective boundary layer must be provided on each side of the recording layer in contact with it. The boundary layers can prevent the deterioration, caused by repeated overwriting, of certain characteristics. The reason is considered to be that the layers act as barrier layers for preventing the diffusion of atoms from the dielectric layers onto the recording layer. Furthermore, the boundary layers improve the erasure characteristics. It is considered that the boundary layers raise the crystallization rate, so improving the erasure characteristics. Furthermore, the boundary layers can also improve the storage durability, i.e., the reproduction characteristics and the overwriting characteristics after long-term storage. The reason is estimated to be that the change of state such as atomic arrangement in the recording layer and the reaction between the dielectric layers and the recording layer can be prevented even if the recording medium is allowed to stand for a long time.

[0029] The first boundary"layer and the second boundary layer are respectively mainly composed of at least one of carbon, carbides, oxides and nitrides. In this case, "mainly composed of" means that the ingredient concerned is present in an amount of 50 wt% or more, by weight of the total weight of the particular layer. It is more preferable that the amount is 80 wt% or more. The carbides, oxides and nitrides may be the carbides, oxides and nitrides of the elements belonging to any of groups 3 to 14 inclusive of the 3rd - 6th period inclusive of the periodic table. In particular, the carbide, oxide or nitride of a metal selected from Al, Si, Sc, Ti, V, Cr, Mn, Fe, CO, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, La, Hf, Ta, W, Re, Ir, Pt, Au, Tl and Pb is preferably used. Especially the carbide, oxide or nitride of a metal selected from Si, Ge, Ti, Zr, Ta, Hb, Hf, Al, Y, Cr, W, Zn, In and Sn is preferably used.

[0030] As the material of the first boundary layer, a material mainly composed of carbon is especially preferable, and in this case, the long-term storage stability of recorded marks can be improved. If a recording layer good in long-term

storage stability, as described later, is used, even a material mainly composed of at least one of carbides, oxides and nitrides can provide good long-term storage stability. The material of the second boundary layer may be the same as or different from the material of the first boundary layer. Having regard to long-term storage stability, it is preferable that the first boundary layer and the second boundary layer are respectively mainly composed of carbon.

[0031] Furthermore, for repetition durability improvement, it is also preferable that the first boundary layer and the second boundary layer are respectively mainly composed of a nitride. Especially a material mainly composed of GeN_x is preferable since it is excellent in the adhesion to the recording layer, and it is more preferable that the x is in a range of $0.8 \leq x \leq 1.33$. It is also preferable to add at least one of Cr, Ti, Mn, Zr, Nb, Mo, Ta, Fe, Co, Ni, Y and La, since the effect of inhibiting the oxidation of Ge for improving the long-term storage stability can be expected. In $GeCr_y$ nitrides, it is preferable that the y is in a range of $0 \leq y \leq 0.5$, and $GeCr_{0.25}$ nitride is especially preferable.

[0032] It is preferable that the thickness of each of the boundary layers is 0.5 nm to 10 nm, having regard to the unlikelihood of delamination and optical conditions. If the thickness is more than 10 nm, the boundary layer is likely to be delaminated from the first dielectric layer or the recording layer. If less than 0.5 nm, it is difficult to form the layer with a uniform thickness by vapor deposition, and the effect of forming the boundary layers may not be obtained. If the boundary layer is mainly composed of carbon, it is especially preferable that the thickness is 0.5 nm to 4 nm, for improved repetition characteristics and long-term storage stability. It can be considered that delamination at the interface is unlikely to occur since the carbon layer is relatively strongly bonded to the adjacent Ge-Sb-Te recording layer and the $ZnS\text{-}SiO_2$ dielectric layer by chemical bonding or similar interaction. However, if the thickness of the carbon layer is too large, the weak graphite sub-layer existing about the center in the normal direction becomes thick. Hence, it can be considered that this portion may be destroyed, for example, by repeated action, and that a burst error may occur.

[0033] When the carbon layer is formed with sputtering, the introducing gas can be a rare gas such as Ar gas, but hydrogen can also be mixed. Another material can also be mixed with the carbon layer, but to obtain good characteristics, it is preferable that carbon is present in an amount of 80 mol% or more.

[0034] The composition of the recording layer of this invention must be in the range of the following formula:

$$[\{(Ge_{1-k}Sn_k)_{0.5}STe_{0.5}\}_x(Sb_{0.4}Te_{0.6})_{1-x}]_{1-Y}Sb_yA_z$$

where A is an element belonging to any of the groups 3 - 14 inclusive of the 3rd - 6th period inclusive of the periodic table, excluding Ge, Sb and Te, and x, y, z and k are in ranges respectively represented by the following formulae (1) or (2)

$$0.5 \leq x \leq 0.95,\ 0 \leq y \leq 0.08,\ 0 \leq z \leq 0.2,\ k = 0 \tag{1}$$

$$0.5 \leq x \leq 0.95,\ 0.01 \leq y \leq 0.08,\ z = 0,\ 0 \leq k \leq 0.5 \tag{2}$$

[0035] If $x < 0.5$, a sufficient signal intensity cannot be obtained since the reflectance change accompanying the phase change of the recording layer becomes small, and good jitter may not be obtained. If $x > 0.95$, since the crystallization rate becomes low, the erasure characteristics are impaired and the overwriting jitter may be aggravated. If $y > 0.08$, the initial erasure characteristics may be impaired or the overwriting characteristics after long-term storage may be impaired. If $z > 0.2$, since the crystallization rate becomes low, the erasure characteristics may be aggravated, the overwriting jitter may be aggravated, the repetition characteristics may deteriorate considerably due to phase separation, and the overwriting characteristics after long-term storage may be impaired. If $z = 0$ and $y < 0.01$, then, the amorphous stability is low, and the reproduction characteristics after long-term storage may be impaired.

[0036] In the case of $z > 0$, k is zero. If $z = 0$, a composition in which Ge is partially substituted by Sn in a range of $0 \leq k \leq 0.5$ is preferable for better erasure characteristics and better storage durability.

[0037] It is preferable to use a recording layer satisfying the following formula, since better amorphous stability and better long-term storage stability can be obtained.

$$\{(Ge_{0.5}Te_{0.5})_x(Sb_{0.4}Te_{0.6})_{1-x}\}_{1-y-z}Sb_yA_s$$

$$0.5 \leq x \leq 0.95,\ 0.03 \leq y \leq 0.08,\ 0 \leq z \leq 0.2.$$

[0038] In the above-mentioned composition range of the recording layer, it is preferable, for better erasure characteristics, that the molar fraction of Sb in three elements of Ge, Sb and Te in the recording layer is 20% or less, i.e.,

$$0.4(1-x)(l-y)+y<0.2.$$

[0039] Furthermore, the recording layer may also contain nitrogen and oxygen, and the argon used for sputtering may also be present.

[0040] It is preferable that the thickness of the recording layer of this invention is 5 nm to 40 nm. If the thickness of the recording layer is less than the minimum of the above range, deterioration of the recording characteristics by repeated overwriting may be remarkable. If the thickness of the recording layer is more than the maximum of the above range, the migration of the recording layer by repeated overwriting may occur, to remarkably aggravate the jitter. A preferable thickness range of the recording layer is 7 nm to 25 nm, to obtain a moderate cooling rate of the recording layer during recording. Furthermore, for keeping the ratio of the absorptivity of the crystalline region to that of the amorphous region as large as possible for improving the erasure characteristics, it is preferable that the recording layer is thinner. A more preferable thickness range of the recording layer for this purpose is 7 nm to 17 nm.

[0041] In a recording medium embodying this invention, for adjusting, for example, the recording sensitivity, a second dielectric layer may also be provided between the second boundary layer and the reflection layer. The material of the second dielectric layer can be the same as or different from that of the first dielectric layer. It is preferable that the thickness of the second dielectric layer is 2 nm to 50 nm. If the thickness of the second dielectric layer is less than the minimum of the above range, defects such as cracking may be caused, so lowering undesirably the repetition durability. If the thickness of the second dielectric layer is more than the Maximum of the above range, the cooling rate of the recording layer may decline undesirably. The thickness of the second dielectric layer may directly affect the cooling of the recording layer, and to obtain better erasure characteristics and repetition durability, a thickness of 30 nm or less is more effective. It is also preferable that the second dielectric layer is formed with a semi-transparent material, since it can absorb light, for using it as thermal energy efficiently for recording and erasure. For example, a mixture consisting of ZnS, SiO_2 and carbon is preferable since the residual stress of the film is small and since deterioration of recording sensitivity, carrier-to-noise ratio (C/N), erasure rate, etc. is unlikely to occur even if recording and erasure are repeated.

[0042] In a recording medium embodying this invention, the absorption correction layer is provided between the second boundary layer or a second dielectric layer and the reflection layer. As described before, in a conventional construction, the light absorptivity of the recording layer of the amorphous state becomes larger than the light absorptivity of the recording layer of the crystalline state. However, the newly provided absorption correction layer can decrease the light absorptivity of the recording layer of the amorphous state, to lessen the difference between the light absorption of the amorphous state and that of the crystalline state and furthermore to make the light absorption of the amorphous state even smaller than that of the crystalline state. The effect of adsorption correction reduces the difference in the temperature rise during recording between the crystalline region and the amorphous region, to reduce the deformation and displacement of recorded marks. Hence, the erasure characteristics and the overwriting jitter can be improved. The absorption correction effect is determined by the thickness and optical constants (refractive index and attenuation coefficient) of respective layers, and especially depends on the optical constants of the absorption correction layer. It is necessary that the refractive index and the attenuation coefficient of the absorption correction layer are adequate, and it is necessary that the refractive index is 1.0 to 4.0 while the attenuation coefficient is 0.5 to 3.0. In this case, the recording medium can be designed to keep the reflectance difference due to phase change large and to keep the absorption correction effect large. It is preferable to measure the refractive index and the attenuation coefficient at the wavelength of the laser beam used for recording or reproduction. It is most preferable to measure it at 660 nm.

[0043] The material preferably used for the absorption correction layer of this invention is a material mainly composed of at least one of compounds of various alloys and metals, and mixtures thereof, particularly, for example, solid solution alloys, intermetallic compounds, oxides, carbides and nitrides respectively containing at least one of silicon, germanium, titanium, zirconium, tungsten, chromium, molybdenum and aluminum. Especially the oxide or nitride of at least one of aluminum and chromium is preferable since it is easy to control optical constants. Especially an aluminum oxide, i.e., AlO_x with x in a range of 0.3 to 0.8 is preferable since the absorption correction layer can have moderate optical constants. A material with 10 wt% or less of a metal such as chromium or titanium or the oxide thereof mixed in an aluminum oxide is also preferable because of such effects as corrosion resistance improvement.

[0044] It is preferable that the thickness of the absorption correction layer is 1 nm or more for improved light absorption correction effect and 200 nm or less in view of productivity. The thickness of the absorption correction layer depends on the optical constants of the absorption correction layer, but a thickness range of 10 nm to 100 nm is preferable.

[0045] The materials that can be used for the reflection layer include metals and alloys and mixtures of metals and metal compounds respectively capable of reflecting light. In particular, metals with high reflectance such as Al, Au, Ag and Cu, alloys mainly composed of them, and metal compounds such as nitrides, oxides and chalcogenated com-

pounds of Al, Si, etc. are preferable. Especially metals such as Al, Au and Ag and alloys mainly composed of them are preferable since high reflectance and high thermal conductivity can be obtained. Especially alloys mainly composed of Al or Ag are preferable since the material cost can be kept low. The thickness of the reflection layer is usually about 10 nm to 300 nm. A range of 30 nm to 200 nm is preferable since high recording sensitivity and large reproduced signal intensity can be obtained.

[0046] A method for producing an optical recording medium of this invention is described below. The method for forming the first dielectric layer, first boundary layer, recording layer, second boundary layer, second dielectric layer, absorption correction layer, reflection layer, etc. on a substrate can be a thin film forming method in vacuum, for example, vacuum evaporation, ion plating or sputtering. Especially for easy control of composition and layer thickness, sputtering is preferable. The thickness of the recording layer formed can be controlled by monitoring the deposition state using a quartz oscillator thickness meter.

[0047] After the reflection layer is formed, a dielectric layer of, e.g. ZnS, SiO_2 or ZnS-SiO_2, or a protective layer made of, e.g., an ultraviolet light curing resin, can be formed as required for preventing flawing and deformation of the optical recording medium, as far as the effects of this invention are not remarkably impaired.

[0048] Furthermore, an optical recording apparatus of this invention has an optical head capable of irradiating with a laser beam, and the above-mentioned optical recording medium is irradiated with the laser beam from the optical head, to record, erase and reproduce information by the reversible phase change between the amorphous phase and the crystalline phase in the optical recording medium.

[0049] For high density recording, it is preferable that the wavelength of the laser beam is in a range from 645 nm to 660 nm. The laser beam wavelengths used for recording, erasing and reproducing information can be respectively equal or different. For high linear velocity recording, it is preferable that the linear velocity of laser beam irradiation is $7.5 \times 10^6 \times d$ (d is the laser beam diameter on the recording surface) or more per second.

[0050] For high density recording, it is preferable that the information recording method is the mark edge method. Furthermore, it is preferable that the length of the shortest mark of the recorded marks recorded by the mark edge method in the laser beam propagation direction is $0.55 \times d$ or less. Moreover, it is preferable that the track width is $0.7 \times d$ or less.

[0051] Especially preferred embodiments of the invention are described in more detail with reference to the following Examples.

(Analyzing and measuring methods)

[0052] The compositions of the reflection layer and the recording layer were confirmed by ICP emission analysis (analyser produced by Seiko Denshi Kogyo K.K.). The composition of the absorption correction layer was confirmed by Rutherford backward scattering analysis. The thickness of the recording layer, dielectric layer and reflection layer during formation were monitored using a quartz oscillator thickness meter. The thickness of each layer was measured by observing the section with a scanning or transmission electron microscope.

[0053] For the optical recording medium having the respective layers formed by sputtering, the recording layer on the entire dish surface was crystallized and initialized by a semiconductor laser beam with a wavelength of 830 nm before recording.

[0054] The recording properties were evaluated by executing mark edge recording according to the 8-16 modulation method using an optical head with an objective numerical aperture of 0.6 and a semiconductor laser wavelength of 660 nm (laser beam diameter 0.95 μm) at a linear velocity of 8.2 m/sec. The recording laser waveform was a general multi-pulse waveform, and a pattern adapted recording compensation method in which the recording pulse edge position was changed in response to the length of a recorded mark and the lengths of the spaces before and after it was adopted. The recording power and the erasing power were set at optimum values in each optical recording medium. The reproducing power was 1.0 mW.

[0055] The reflectance was obtained from the reproduction signal potential at the mirror portion of the optical recording medium.

[0056] The erasure characteristics were evaluated as described below. At first, a recording frequency of 2.7 MHz, the longest recording mark (11T mark) was overwritten 10 times in'the groove, and on it, at a recording frequency of 9.7 MHz, the shortest recording mark (3T mark, 0.42 μm in the length in the laser beam propagation direction) was overwritten once. With the ratio of the carrier of the shortest recorded mark to the carrier of the longest recorded mark after overwriting as the effective erasure rate, it was measured using a spectrum analyzer at a band width of 30 kHz.

[0057] Then, a random pattern was overwritten on the groove 100 times, and the jitter was measured using a time interval analyzer. In succession, a random pattern was overwritten on the adjacent tracks on both sides 100 times each and erased, and the jitter of the central track was measured again, to evaluate the rise of jitter caused by the cross erasure.

[0058] Furthermore, the durability against reproducing light deterioration was evaluated by measuring the change

of jitter after reproducing a recorded track at a reproducing power of 1.2 Mw repetitively 1000 times.

[0059] The repetition durability was evaluated by measuring the jitter after overwriting 100,000 times on the groove. Furthermore, the decline of the amplitude of signal waveform and the presence of burst defect were also observed using an oscilloscope.

[0060] The storage durability was evaluated by recording using a drive for evaluation capable of measuring the byte error rate, storing the recording medium in a 80°C or 90°C oven for an acceleration test, and evaluating the signal reproduction characteristics and the overwriting characteristics in reference to the byte error rates.

(Example 1)

[0061] A polycarbonate substrate having a spiral groove with a thickness of 0.6 mm and a diameter of 12 cm at a pitch of 1.23 μm (land width 0.615 μm and groove width of 0.615 μm) was revolved at 40 rpm and was coated with layers by sputtering. At first, a vacuum vessel was evacuated to 1 x 10^{-4} Pa, and a ZnS target with 20 mol% of SiO_2 added was sputtered in 0.2 Pa argon gas atmosphere, to form a 135 nm thick first dielectric layer (refractive index 2.1, attenuation coefficient 0) on the substrate. Then, a carbon target was sputtered, to form a 2 nm carbon layer as the first boundary layer. In succession, an alloy target consisting of Ge, Sb and Te was sputtered to form a 10 nm thick recording layer of composition $Ge_{28.6}Sb_{17.8}Te_{53.6}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.579}(Sb_{0.4}Te_{0.6})_{0.421}\}_{0.989}Sb_{0.011}$. Furthermore, a 2 nm thick germanium nitride layer ($GeN_{1.2}$) was formed as the secondary boundary layer by sputtering a germanium target using a mixed gas consisting of argon and nitrogen. In succession, a 26 nm thick second dielectric layer was formed by sputtering the same $ZnS-SiO_2$ target as used for the first dielectric layer. Moreover, as the absorption correction layer, an aluminum target was sputtered using a mixed gas consisting of argon and oxygen, to form a 50 nm thick aluminum oxide layer ($AlO_{0.41}$, refractive index 2.2, attenuation coefficient 2.1). In succession, $Al_{97.5}Cr_{2.5}$ alloy was sputtered, to form a 90 nm thick reflection layer. The disc was taken out of the vacuum vessel, and on the reflection layer, an acrylic ultraviolet light curing resin (SD-101 produced by Dainippon Ink & Chemicals, Inc.) was applied by spin coating, and cured by ultraviolet light irradiation, to form a 3 μm thick resin layer. Then, a slow-acting ultraviolet light curing resin was applied using a screen printing machine, and irradiated with ultraviolet light. The disc was joined with another disc produced similarly, to obtain an optical recording medium of this invention. The difference between the reflectance of the recording layer in the crystalline state and that in the amorphous state was 20%, to show that a sufficient contrast could be secured. According to optical calculation at a wavelength of 660 nm, the ratio of the light absorptivity of the crystalline region of the recording layer to that of the amorphous region (Ac/Aa) was 1.0, to show that an absorption-correction effect could be obtained. The effective erasure rate measured was 28 dB, to show good erasure characteristics. The jitter after overwriting 100 times was very good, at a window width of 7.7%. The jitter containing the influence of cross erasure due to the repeated, recording on the adjacent tracks was 7.9%, showing a small rise of jitter due to the cross erasure. Furthermore, reproducing light deterioration was, not observed. The jitter after overwriting 100,000 times was practically sufficiently small, at 9.8%. The signal amplitude changed little as compared with the signal amplitude after overwriting 100 times, and no burst defect was observed either. That is, it was found that there was no problem with the repetition durability.

[0062] The optical recording medium was used for recording once, and the byte error rate measured in this case was 1.0 x 10^{-5}. The optical recording medium as recorded was allowed to stand in air not adjusted in humidity by humidification, etc. at 80°C for 100 hours. Then, the byte error rate of the same portion was measured and found to be 1.6 x 10^{-5}, showing little change, to show that the reproduction characteristics after long-term storage were good. Furthermore, overwriting was executed once on the same portion, and the byte error was found to be 3.2 x 10^{-5}, and it could be confirmed that the overwriting characteristics after long-term storage were also good enough. Moreover, the same optical recording medium was allowed to stand at 90°C at 80% relative humidity for 140 hours, but no burst defect due to delamination was observed. That is, it was confirmed that the storage durability was good.

(Example 2)

[0063] An optical recording medium similar to that of Example 1 except that a 2 nm thick germanium nitride layer ($GeN_{1.2}$) was formed as the first boundary layer was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 3)

[0064] An optical recording medium similar to that of Example 2 except that the composition of the recording layer was $Ge_{28.8}Sb_{18.8}Te_{532.4}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.594}(Sb_{0.4}Te_{0.6})_{0.406}\}_{0.969}Sb_{0.031}$ was prepared and evaluated. As shown in Table 2, it was confirmed that

all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 4)

[0065] An optical recording medium similar to that of Example 1 except that a 2 nm thick carbon layer was formed as the second boundary layer was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 5)

[0066] An optical recording medium similar to that of Example 3 except that 2 nm thick germanium chromium nitride layers ($GeCr_{0.25}N_{1.2}$) were formed as the first and boundary layers by sputtering a $GeCr_{0.25}$ target using a mixed gas consisting of argon and nitrogen was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 6)

[0067] An optical recording medium similar to that of Example 1 except that an alloy target consisting of Ge, Sn, Sb and Te was sputtered to form a 10 nm thick layer with composition, $Ge_{22.2}Sn_{7.4}Sb_{17.1}Te_{53.3}$, i.e., $[\{(Ge_{0.75}Sn_{0.25})_{0.5}Te_{0.5}\}_{0.60}(Sb_{0.4}Te_{0.6})_{0.40}]_{0.987}Sb_{0.013}$ was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light, deterioration, repetition durability and storage durability were good.

(Example 7)

[0068] An optical recording medium similar to that of Example 3 except that 2 nm thick aluminum oxide layers were formed as the first and second boundary layers by sputtering an aluminum oxide target using argon gas was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 8)

[0069] An optical recording medium similar to that of Example 3 except that 2 nm thick silicon carbide layers were formed as the first and second boundary layers by sputtering a silicon carbide target using argon gas was prepared and evaluated. As shown In Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 9)

[0070] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{36}Sb_{12}Te_{52}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.733}(Sb_{0.4}Te_{0.6})_{0.267}\}_{0.987}Sb_{0.013}$ was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 10)

[0071] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{28.3}Sb_{16.9}Te_{53.8}Nb_1$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.572}(Sb_{0.4}Te_{0.6})_{0.428}\}Nb_{0.01}$ was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

[0072] Also, when each of Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, La, Hf, Ta, W, Re, Ir, Pt, Au, Tl or Pb was used instead of Nb in the composition of the recording layer, almost similar results could be obtained.

(Example 11)

[0073] An optical recording medium similar to that of Example 1 except that a 50 nm thick aluminum oxide layer ($AlO_{0.64}$, refractive index 2.8, attenuation coefficient 1.5) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and oxygen was prepared and evaluated.

[0074] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 12)

[0075] An optical recording medium similar to that of Example 1 except that a 50 nm thick chromium nitride layer ($CrN_{0.74}$, refractive index 3.2, attenuation coefficient 2.3) was formed as the absorption correction layer by sputtering a chromium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0076] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 13)

[0077] An optical recording medium similar to that of Example 1 except that a 50 nm thick chromium nitride layer ($CrN_{0.91}$, refractive index 3.5, attenuation coefficient 1.7) was formed as the absorption correction layer by sputtering a chromium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0078] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 14)

[0079] An optical recording medium similar to that of Example 1 except that a 50 nm thick aluminum nitride layer (AlN, refractive index 2.2, attenuation coefficient 2.0) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0080] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 15)

[0081] An optical recording medium similar to that of Example 3 except that 2 nm thick germanium nitride layers ($GeN_{0.8}$) were formed as the first and second boundary layers by sputtering a germanium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 16)

[0082] An optical recording medium similar to that of Example 3 except that 2 nm thick germanium chromium nitride layers ($GeCr_{0.25}N_{0.8}$) were formed as the first and second boundary layers by sputtering a $GeCr_{0.25}$ target using a mixed gas consisting of argon and nitrogen was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 17)

[0083] An optical recording medium similar to that of Example 3 except that 2 nm thick germanium chromium nitride layers ($GeCr_{0.2}N_{1.2}$) were formed as the first and second boundary layers by sputtering a $GeCr_{0.2}$ target using a mixed gas consisting of argon and nitrogen was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 18)

[0084] An optical recording medium similar to that of Example 3 except that 2 nm thick germanium chromium nitride layers ($GeCr_{0.4}N_{1.2}$) were formed as the first and second boundary layers by sputtering a $GeCr_{0.4}$ target using a mixed gas consisting of argon and nitrogen was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 19)

[0085] As described for Example 1, a 120 nm thick ZnS-SiO_2 layer was formed as the first dielectric layer on the substrate, and a 2 nm thick carbon layer was formed as the first boundary layer. In succession, a 9 nm thick recording layer of composition $Ge_{36}Sb_{12}Te_{52}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.733}(Sb_{0.4}Te_{0.6})_{0.267}\}_{0.987}Sb_{0.013}$ was formed, and furthermore a 2 nm thick carbon layer was formed as the second boundary layer. In succession, a 35 nm thick ZnS-SiO_2 layer was formed as the second dielectric layer, and a 70 nm thick aluminum oxide layer ($AlO_{0.41}$, refractive index 2.2, attenuation coefficient 2.1) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and oxygen. In succession, a 90 nm thick reflection layer was formed by sputtering $Al_{97.5}Cr_{2.5}$ alloy.

[0086] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 20)

[0087] An optical recording medium similar to Example 19 except that a 50 nm thick chromium nitride ($CrN_{0.74}$, refractive index 3.2, attenuation coefficient 2.3) was formed as the absorption correction layer by sputtering a chromium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0088] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 21)

[0089] As described for Example 1, a 70 nm thick ZnS-SiO_2 layer was formed as the first dielectric layer on the substrate, and a 2 nm thick carbon layer was formed as the first boundary layer. In succession, a 12 nm thick recording layer of composition $Ge_{36}Sb_{12}Te_{52}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.733}(Sb_{0.4}Te_{0.6})_{0.267}\}_{0.987}Sb_{0.013}$ was formed, and furthermore a 2 nm thick carbon layer was formed as the second boundary layer. In succession, a 15 nm thick ZnS-SiO_2 layer was formed as the second dielectric layer, and a 50 nm thick aluminum oxide layer ($AlO_{0.64}$, refractive index 2.8, attenuation coefficient 1.5) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and oxygen. In succession, a 90 nm thick reflection layer was formed by sputtering $Al_{97.5}Cr_{2.5}$ alloy.

[0090] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 22)

[0091] An optical recording medium similar to Example 21 except that a 50 nm thick chromium nitride layer ($CrN_{0.91}$, refractive index 3.5, attenuation coefficient 1.7) was formed as the absorption correction layer by sputtering a chromium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0092] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 23)

[0093] An optical recording medium similar to that of Example 22 except that the composition of the recording layer was $Ge_{35}Sb_{14}Te_{51}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.733}(Sb_{0.4}Te_{0.6})_{0.267}\}_{0.967}Sb_{0.033}$, and that 2 nm thick germanium nitride layers ($GeN_{1.2}$) were formed as the first and second boundary layers by sputtering a germanium target using a mixed gas consisting of argon and nitrogen was prepared and evaluated.

[0094] As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light

deterioration, repetition durability and storage durability were good.

(Example 24)

[0095] An optical recording medium similar to that of Example 23 except that 2 nm aluminum oxide layers were formed as the first and second boundary layers by sputtering an aluminum oxide target using argon gas was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 25)

[0096] An optical recording medium similar to that of Example 23 except that 2 nm silicon carbide layers were formed as the first and second boundary layers by sputtering a silicon carbide target using argon gas was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Example 26)

[0097] An optical recording medium similar to that of Example 22 except that the composition of the recording layer was $Ge_{36.3}Sb_{10.6}Te_{52.1}Nb_1$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.733}(Sb_{0.4}Te_{0.6})_{0.267}\}_{0.99}Nb_{0.01}$ was prepared and evaluated. As shown in Table 2, it was confirmed that all of erasure characteristics, jitter, cross erasure, reproducing light deterioration, repetition durability and storage durability were good.

(Comparative Example 1)

[0098] An optical recording medium similar to that of Example 1 except that the first and second boundary layers were not formed was prepared and evaluated. The effective erasure rate was 15 dB, being very poor compared to that of Example 1. Hence, the overwriting jitter was also aggravated, and the jitter after recording 100 times became as large as 11.5%. After overwriting 100,000 times, the reproduced signal amplitude declined, and the jitter was as large as 18%, causing such problems as error rate increase.

[0099] Furthermore, this disc was used for recording once, and the byte error rate in this case was measured and found to be 3.0×10^{-5}. The disc as recorded was allowed to stand in air not adjusted in humidity by humidification, etc. at 80°C for 100 hours. Then, the byte error rate of the same portion was measured and found to be 3.9×10^{-5}, showing little change. However, when overwriting was executed once on this portion, the byte error rate was 4.3×10^{-3}, showing that the overwriting characteristics after long-term storage were very poor.

(Comparative Example 2)'

[0100] An optical recording medium similar to that of Example 1 except that the absorption correction layer was not formed was prepared and evaluated. However, to optimize the optical conditions, the thickness of the first dielectric layer, recording layer and second dielectric layer were 160 nm, 12 nm and 17 nm respectively.

[0101] The ratio of the light absorptivity of the crystalline region of the recording layer to that of the amorphous region (Ac/Aa) at a wavelength of 660nm was 0.8, and since no absorption correction layer was formed, the light absorptivity ratio was small. The effective erasure rate was 21 dB, being poor compared to that of Example 1. The jitter after recording 100 times was 8.7%, and the jitter containing the influence of cross erasure by repeated recording on the adjacent tracks was 9.7%, to show that the jitter rise affected by the cross erasure was large. Furthermore, the track used for recording 100 times was used for reproducing repetitively 1000 times, and the jitter was found to be 13.0%, to show reproducing light deterioration.

[0102] As shown in Table 2, repetition durability and storage durability were good.

(Comparative Example 3)

[0103] An optical recording medium similar to that of Example 1 except that a 50 nm thick titanium layer (refractive index 2.5, attenuation coefficient 3.2) was formed as the absorption correction layer by sputtering a titanium target using argon gas was prepared and evaluated. The light absorptivity ratio (Ac/Aa) at a wavelength of 660 nm was 0.9, being rather smaller than that of Example 1. The effective erasure rate was 23 dB, being rather poor compared to that of Example 1. The jitter after recording 100 times was 8.8%, and the jitter containing the influence of cross erasure by

repeated recording on the adjacent tracks was 9.8%. That is, the jitter rise affected by the cross erasure was large.

[0104] Furthermore, even when each of Ni, W, Mo, V, Nb, Cr or Fe was used instead of Ti as the absorption correction layer, almost similar results were obtained.

(Comparative Example 4)

[0105] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{47.9}Sb_{2.5}Te_{49.6}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.97}(Sb_{0.4}Te_{0.6})_{0.03}\}_{0.987}Sb_{0.013}$ was prepared and evaluated. The effective erasure rate was 13 dB, being very low compared to that of Example 1. Hence, the jitter after recording 100 times was as large as 11.6%.

(Comparative Example 5)

[0106] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{19.7}Sb_{25.0}Te_{55.3}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.40}(Sb_{0.4}Te_{0.6})_{0.60}\}_{0.987}Sb_{0.013}$ was prepared and evaluated. The effective erasure rate was 25 dB, showing good erasure characteristics. However, the difference between the reflectance of the recording layer in the crystalline state and that in the amorphous state was 14%, being small compared to that of Example 1, and the jitter after overwriting 100 times was as large as 9.8%.

(Comparative Example 6)

[0107] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{28.6}Sb_{17.1}Te_{54.3}$, i.e., $(Ge_{0.5}Te_{0.5})_{0.572}(Sb_{0.4}Te_{0.6})_{0.428}$ was prepared and evaluated. As shown in Table 2, erasure characteristics, jitter, cross erasure and repetition durability were good.

[0108] The disc was used for recording once, and the byte error rate in this case was measured and found to be 1.2 x 10^{-5}. The disc as recorded was allowed to stand in air not adjusted in humidity by humidification, etc. at 80°C for 100 hours. Then, the byte error rate of the same portion was measured and found to have remarkably increased to 1.4 x 10^{-3}, to show that the reproduction characteristics after long-term storage were poor.

(Comparative Example 7)

[0109] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{25.7}Sb_{25.4}Te_{48.9}$ i.e., $\{(Ge_{0.5}Te_{0.5})_{0.572}(Sb_{0.4}Te_{0.6})_{0.428}\}_{0.9}Sb_{0.1}$ was prepared and evaluated. The effective erasure rate was 18 dB, being poor compared to that of Example 1.

[0110] The disc was used for recording once, and the byte error rate in this case was measured and found to be 2.3 x 10^{-5}. The disc as recorded was allowed to stand in air not adjusted in humidity by humidification, etc. at 80°C for 100 hours. Then, the byte error rate of the same portion was measured and found to be 3.0 x 10^{-5}, showing little change, hence showing that the reproduction characteristics after long-term storage were good. However, when overwriting was executed once on the same portion, the byte error rate was found to have remarkably increased to 3.4 x 10^{-3}. That is, the overwriting characteristics after long-term storage were poor.

(Comparative Example 8)

[0111] An optical recording medium similar to that of Example 1 except that the composition of the recording layer was $Ge_{20}Sb_{12}Te_{38}Nb_{30}$, i.e., $\{(Ge_{0.5}Te_{0.5})_{0.572}(Sb_{0.4}Te_{0.6})_{0.428}\}_{0.7}Nb_{0.3}$ was prepared and evaluated. The effective erasure rate was 19 dB, being very poor compared to that of Example 1. The jitter after overwriting 100 times was also as large as 10.7% , being poor compared to that of Example 1. After overwriting 100,000 times, the reproduced signal amplitude declined, and the jitter was as large as 17%, causing such problems as error rate increase.

[0112] The disc was used for recording once, and the byte error rate in this case was measured and found to be 8.5 x 10^{-5}. The disc as recorded was allowed to stand in air not adjusted in humidity by humidification, etc. at 80°C for 100 hours. Then, the byte error rate of the same portion was measured and found to be 9.5 x 10^{-5}, showing little change, hence showing that the reproduction characteristics after long-term storage were good. However, when overwriting was executed once on the same portion, the byte error rate was found to have remarkably increased to 8.5 x 10^{-5}. That is, the overwriting characteristics after long-term storage were poor.

(Comparative Example 9)

[0113] An optical recording medium similar to that of Example 1 except that a 50 nm thick aluminum oxide layer ($AlO_{0.25}$, refractive index 2.0, attenuation coefficient 3.5) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and'oxygen but different from that of Example 1 in composition was prepared and evaluated. The light absorptivity ratio (Ac/Aa) at a wavelength of 660 nm was 0.9, being rather small compared to that of Example 1. The effective erasure rate was 21 dB, being rather poor compared to that of Example 1. The jitter after recording 100 times was 8.5% respectively on the land and the groove, and the jitter containing the influence of cross erasure by repeated recording on the adjacent tracks was 9.3%, showing that the jitter rise due to the cross erasure was rather large.

(Comparative Example 10)

[0114] An optical recording medium similar to that of Example 1 except that a 50 nm thick aluminum oxide layer ($AlO_{0.90}$, refractive index 2.2, attenuation coefficient 0.4) was formed as the absorption correction layer by sputtering an aluminum target using a mixed gas consisting of argon and oxygen different from that of Example 1 in composition was prepared and evaluated. The light absorptivity ratio (Ac/Aa) at a wavelength of 660 nmwas 0.8, being small compared to that of Example 1. The effective erasure rate was 18 dB, being poor compared to that of Example 1. The jitter after recording 100 times was 9.0%, and the jitter containing the influence of cross erasure by repeated recording on the adjacent tracks was 10.1%, showing that the jitter rise due to the cross erasure was rather large.

Table 1

	1st boundary layer		Recording layer							2nd boundary layer		Absorption correction layer			
	Composition	Thickness (nm)	Composition	Thickness (nm)	A	x	y	z	k	Composition	Thickness (nm)	Composition	Thickness (nm)	Refractive index	Attenuation coefficient
Example 1	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 2	GeN1.2	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 3	GeN1.2	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 4	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	C	2	AlO 0.41	50	2.2	2.1
Example 5	GeCr0.25N1.2	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeCr0.25N1.2	2	AlO 0.41	50	2.2	2.1
Example 6	C	2	Ge22.2Sn7.4Sb17.1Te53.3	10	---	0.6	0.013	0	0.25	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 7	Al2O3	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	Al2O3	2	AlO 0.41	50	2.2	2.1
Example 8	SiC	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	SiC	2	AlO 0.41	50	2.2	2.1
Example 9	C	2	Ge36Sb12Te52	10	---	0.733	0.013	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 10	C	2	Ge28.3Sb16.9Te53.8Nb1	10	Nb	0.572	0	0.01	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Example 11	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	AlO 0.64	50	2.8	1.5
Example 12	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	CrN 0.74	50	3.2	2.3
Example 13	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	CrN 0.91	50	3.5	1.7
Example 14	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	Al-N	50	2.2	2.0
Example 15	GeN0.8	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeN0.8	2	AlO 0.41	50	2.2	2.1
Example 16	GeCr0.25N0.8	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeCr0.25N0.8	2	AlO 0.41	50	2.2	2.1
Example 17	GeCr0.2N1.2	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeCr0.2N1.2	2	AlO 0.41	50	2.2	2.1
Example 18	GeCr0.4N1.2	2	Ge28.8Sb18.8Te52.4	10	---	0.594	0.031	0	0	GeCr0.4N1.2	2	AlO 0.41	50	2.2	2.1
Example 19	C	2	Ge36Sb12Te52	9	---	0.733	0.013	0	0	C	2	AlO 0.41	70	2.2	2.1
Example 20	C	2	Ge36Sb12Te52	9	---	0.733	0.013	0	0	C	2	CrN 0.74	50	3.2	2.3
Example 21	C	2	Ge36Sb12Te52	12	---	0.733	0.013	0	0	C	2	AlO 0.64	50	2.8	1.5
Example 22	C	2	Ge36Sb12Te52	12	---	0.733	0.013	0	0	C	2	CrN 0.91	50	3.5	1.7
Example 23	GeN1.2	2	Ge35Sb14Te51	12	---	0.733	0.033	0	0	GeN1.2	2	CrN 0.91	50	3.5	1.7
Example 24	Al2O3	2	Ge35Sb14Te51	12	---	0.733	0.033	0	0	Al2O3	2	CrN 0.91	50	3.5	1.7
Example 25	SiC	2	Ge35Sb14Te51	12	---	0.733	0.033	0	0	SiC	2	CrN 0.91	50	3.5	1.7
Example 26	C	2	Ge36.3Sb10.6Te52.1Nb1	12	Nb	0.733	0	0.01	0	C	2	CrN 0.91	50	3.5	1.7
Comparative Example 1	none	---		10	---	0.579	0.011	0	0	none	---	AlO 0.41	50	2.2	2.1
Comparative Example 2	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	none	---	---	---
Comparative Example 3	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	Ti	50	2.5	3.2
Comparative Example 4	C	2	Ge47.9Sb2.5Te49.6	10	---	0.97	0.013	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Comparative Example 5	C	2	Ge19.7Sb25.0Te55.3	10	---	0.4	0.013	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Comparative Example 6	C	2	Ge28.6Sb17.1Te54.3	10	---	0.572	0	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Comparative Example 7	C	2	Ge25.7Sb25.4Te48.9	10	---	0.572	0.1	0	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Comparative Example 8	C	2	Ge20Sb12Te38Nb30	10	Nb	0.572	0	0.3	0	GeN1.2	2	AlO 0.41	50	2.2	2.1
Comparative Example 9	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	AlO 0.25	50	2.0	3.5
Comparative Example 10	C	2	Ge28.6Sb17.8Te53.6	10	---	0.579	0.011	0	0	GeN1.2	2	AlO 0.9	50	2.2	0.4

Table 2

	Reflectance difference (%)	Ac/Aa	effective erasure rate (dB)	Jitter after overwriting 100 times (%)	Jitter after cross erasure test (%)	Reproducing light deterioration	Characteristics after overwriting 100,000 times			Byte error rate after recording once (x10⁻⁵)	Characteristics after long-term storage		
							Jitter (%)	Signal amplitude	Burst defect		Byte error rate (x10⁻⁵)	Byte error rate due to overwriting (x10⁻⁵)	Burst defect
Example 1	20	1.8	28	7.7	7.9	Not observed	9.8	No change	Not observed	1.0	1.6	3.2	Not observed
Example 2	20	1.0	28	7.8	8.0	Not observed	9.3	No change	Not observed	1.2	12	17	Not observed
Example 3	20	1.0	25	8.3	8.6	Not observed	9.2	No change	Not observed	2.0	5.6	9.0	Not observed
Example 4	20	1.0	25	8.1	8.4	Not observed	10.5	No change	Not observed	2.0	2.0	3.6	Not observed
Example 5	20	1.0	25	8.2	8.5	Not observed	9.3	No change	Not observed	1.8	3.6	7.2	Not observed
Example 6	19	1.0	28	7.9	8.1	Not observed	9.7	No change	Not observed	1.0	1.8	2.7	Not observed
Example 7	20	1.0	25	8.3	8.6	Not observed	11.0	No change	Not observed	2.0	6.4	18	Not observed
Example 8	20	1.0	24	8.4	8.7	Not observed	11.5	No change	Not observed	3.0	11	25	Not observed
Example 9	23	1.0	24	8.3	8.6	Not observed	10.0	No change	Not observed	2.5	4.5	11	Not observed
Example 10	20	1.0	27	8.1	8.4	Not observed	9.9	No change	Not observed	1.9	3.8	8.7	Not observed
Example 11	22	1.0	24	8.4	8.8	Not observed	10.3	No change	Not observed	3.2	6.1	12	Not observed
Example 12	19	1.2	25	8.2	8.5	Not observed	10.1	No change	Not observed	2.2	4.0	9.6	Not observed
Example 13	20	1.1	24	8.4	8.9	Not observed	10.5	No change	Not observed	3.0	5.1	11	Not observed
Example 14	20	1.0	24	8.3	8.7	Not observed	9.8	No change	Not observed	2.5	5.0	11	Not observed
Example 15	20	1.0	25	8.3	8.6	Not observed	10.3	No change	Not observed	2.0	4.4	7.9	Not observed
Example 16	20	1.0	25	8.2	8.5	Not observed	10.1	No change	Not observed	2.0	3.6	7.2	Not observed
Example 17	20	1.0	25	8.2	8.5	Not observed	9.3	No change	Not observed	2.0	9.0	9.0	Not observed
Example 18	20	1.0	25	8.2	8.5	Not observed	10.1	No change	Not observed	2.0	3.4	7.8	Not observed
Example 19	19	1.2	28	8.3	8.6	Not observed	11.0	No change	Not observed	1.5	2.5	4.1	Not observed
Example 20	18	1.2	28	8.4	8.7	Not observed	11.0	No change	Not observed	1.5	2.5	4.1	Not observed
Example 21	20	1.1	25	9.3	9.7	Not observed	11.0	No change	Not observed	2.0	2.8	5.0	Not observed
Example 22	19	1.2	28	9.0	9.3	Not observed	11.0	No change	Not observed	2.5	3.0	4.1	Not observed
Example 23	21	1.2	28	8.8	9.1	Not observed	10.0	No change	Not observed	2.3	3.2	4.5	Not observed
Example 24	21	1.0	25	9.0	9.4	Not observed	11.3	No change	Not observed	2.0	4.0	9.2	Not observed
Example 25	21	1.0	25	9.0	9.4	Not observed	11.3	No change	Not observed	2.0	7.0	18	Not observed
Example 26	21	1.0	27	9.2	9.5	Not observed	12.0	No change	Not observed	2.0	2.6	3.1	Not observed
Comparative Example 1	20	1.0	15	11.5			18.0	Declined	Not observed	3.0	3.9	430	
Comparative Example 2	24	0.8	21	8.7	9.7	Observed	10.8	No change	Not observed	3.5	7.4	18	Not observed
Comparative Example 3	21	0.9	23	8.8	9.8								
Comparative Example 4	22		13	11.6									
Comparative Example 5	14		25	9.8									
Comparative Example 6	20		28	8.0	8.2		10.1	No change		1.2	140		
Comparative Example 7	20		18	8.9						2.3	3.0	340	
Comparative Example 8	20		19	10.7			17.0	Declined		8.5	9.5	850	
Comparative Example 9	19	0.9	21	8.5	9.3								
Comparative Example 10	21	0.8	18	9.0	10.1								

Industrial Applicability

[0115] Rewritable phase change type optical recording media and optical recording apparatus embodying the invention are good in erasure characteristics and small in jitter even in high linear velocity high density recording, are unlikely to cause cross erasure even in the use of a substrate with a narrow track width, are unlikely to deteriorate in signal quality even after repeated irradiation with a laser beam, and are good also in storage durability. Optical recording media embodying this invention are also excellent in repetition durability.

Claims

1. An optical recording medium which allows information to be recorded, erased and reproduced by laser beam irradiation, and in which the recording and erasure of information are achieved by reversible phase change between an amorphous phase and a crystalline phase, characterized in that at least a first dielectric layer, a first boundary layer, a recording layer, a second boundary layer, an absorption correction layer and a reflection layer are provided in that order on a substrate, that the composition of the recording layer is represented by general formula

$$[\{(Ge_{1-k}Sn_k)_{0.5}Te_{0.5}\}_x(Sb_{0.4}Te_{0.6})_{1-x}]_{1-y}Sb_yA_z$$

where A is an element belonging to any of the groups 3 - 14 inclusive of the 3rd - 6th period inclusive of the periodic table, excluding Ge, Sb and Te; and x, y, z and k are in ranges respectively represented by the following formulae (1) or (2)

$$0.5 \leq x \leq 0.95,\ 0 \leq y \leq 0.08,\ 0 < z \leq 0.2,\ k = 0 \quad (1)$$

$$0.5 \leq x \leq 0.95,\ 0.01 \leq y \leq 0.08,\ z = 0,\ 0 \leq k \leq 0.5 \quad (2)$$

that the first boundary layer and the second boundary layer are respectively mainly composed of at least one of carbon, carbides, oxides and nitrides, and that the absorption correction layer has a refractive index of 1.0 to 4.0 and an attenuation coefficient of 0.5 to 3.0.

2. An optical recording medium according to claim 1, wherein the first boundary layer is a layer mainly composed of carbon.

3. An optical recording medium according to claim 2, wherein the first boundary layer and the second boundary layer are layers mainly composed of carbon.

4. An optical recording medium according to claim 1, wherein the first boundary layer and the second boundary layer are layers mainly composed of at least one of carbides, oxides and nitrides, and the composition of the recording layer is represented by the following formula:

$$\{(Ge_{0.5}Sn_{0.5})_x(Sb_{0.4}Te_{0.6})_{1-x}\}_{1-y-z}Sb_yA_z$$

where A is an element belonging to any of the groups 3 - 14 inclusively of the 3rd - 6th period inclusively of the periodic table, excluding Ge, Sb and Te, and x, y and z are in the ranges respectively represented by the following formulae:

$$0.5 \leq x \leq 0.95,\ 0.03 \leq y \leq 0.08,\ 0 \leq z \leq 0.2.$$

5. An optical recording medium according to any preceding claim, wherein the absorption correction layer is made of a material mainly composed of the oxides or nitrides of metals containing at least one of Al and Cr.

6. An optical recording medium according to claim 5, wherein the absorption correction layer is mainly composed of

AlO_x (x = 0.3 to 0.8).

7. An optical recording medium according to any preceding claim, wherein the first dielectric layer has a refractive index of 1.9 to 2.4 and an attenuation coefficient of 0.1 or less.

8. An optical recording medium according to any preceding claim, wherein the thickness of the first dielectric layer is 50 nm to 200 nm; the thickness of the recording layer is 7 nm to 17 nm; and the thickness of the absorption correction layer is 10 nm to 100 nm.

9. An optical recording medium according to any preceding claim, wherein the refractive index and the attenuation coefficient are measured at the wavelength of the laser beam used for recording or reproduction.

10. An optical recording medium according to any one of claims 1 to 8, wherein the refractive index and the attenuation coefficient are measured at a laser beam wavelength of 660 nm.

11. An optical recording apparatus having an optical head and an optical recording medium, in which a laser beam is applied from the optical head to allow information to be recorded, erased and reproduced by reversible phase change between an amorphous phase and a crystalline phase in the optical recording medium, characterized in that the linear velocity of laser beam irradiation is $7.5 \times 10^6 \times d$ (d is the laser beam diameter on the recording surface) or more per second, that the length of the shortest mark of the recorded marks recorded according to the mark edge method by the laser beam is $0.55 \times d$ or less in the laser beam propagation direction, that the track width of the optical recording medium is $0.7 \times d$ or less, and that the optical recording medium is an optical recording medium according to any one of claims 1 to 10.

12. An optical recording apparatus according to claim 11, wherein each of the wavelengths of the laser beams used for recording, erasure and reproduction is within the range 645 to"660 nm inclusive.